Umklapp-Mediated Quantization of Electronic States in Ag Films on Ge(111)

S.-J. Tang,[1] Y.-R. Lee,[1,2] S.-L. Chang,[2] T. Miller,[1] and T.-C. Chiang[1]

[1]*Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA, and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois, 61801-2902, USA*

[2]*National Tsing Hua University, 101, Section 2, Kuang Fu Road, Hsinchu, Taiwan 30013, Republic of China*

(Received 25 March 2006; published 2 June 2006)

We employ angle-resolved photoemission to study the electronic structure of atomically uniform films of Ag grown on Ge(111). A new kind of quantum well state is observed near a specific emission direction away from the surface normal. In contrast with the usual quantum well state arising from electron confinement by specular reflections at the surface and interface of the film, the new kind involves retroreflections, or umklapp reflections, at the interface. It requires four reflections, instead of the usual two reflections, to complete a coherent interference path.

DOI: 10.1103/PhysRevLett.96.216803 PACS numbers: 73.21.Fg, 68.65.Fg, 79.60.Dp

Electrons in a thin film on a substrate can be confined by the substrate potential to form discrete states, known as quantum well states [1–6]. As discussed in the literature, such states generally involve specular (mirrorlike) reflections at the film surface and the interface, and are analogues to the standing wave modes found in an optical Fabry-Pérot interferometer formed by two parallel mirrors [7]. Here we report on the discovery of a new kind of quantum well state (referred to, below, as the second kind) in thin Ag films grown on Ge(111). In this case, the reflections at the interface are retroreflections (umklapp reflections [8]) that reverse the directions of incident electrons at an oblique angle rather than bounce the electrons off to directions symmetric with respect to the surface normal. As observed by angle-resolved photoemission, the retroreflections cause these new states to have a characteristic photoelectron emission pattern that is centered about directions away from the surface normal, providing a clear experimental distinction from the usual states. Quantum well effects can substantially influence the properties of thin films, often resulting in their extreme sensitivity to changes in film thickness. Indeed, large variations as a function of film thickness in thermal stability [9], work function [10], electron-phonon coupling [11,12], and superconducting transition temperatures [13–16] have been reported. Implications abound regarding nanoscale materials and device technologies. The discovery reported herein necessitates a rethinking of the overall quantum electronic structure and its relationship to properties and functionality of thin film systems.

A ray diagram presented in the top panel of Fig. 1 illustrates the basic idea for a quantum well state of the usual kind. Two consecutive specular reflections (*S* reflections), one at the surface and the other at the interface, lead to a closed interference path. The result is a standing wave, or a quantum well state, when the wavelength of the electron is compatible with the interference path length. Quantum well states of the second kind are schematically illustrated by the ray diagram in the lower panel of Fig. 1. For the case studied, Ag on Ge(111), the Ag is essentially a jellium, consisting of a sea of nearly free electrons. Its surface behaves like a smooth mirror that reflects electrons specularly. The interface, however, has a corrugation potential derived from the fairly rigid surface structure of Ge(111). This potential acts as a diffraction grating. Electrons in the film impinging upon the interface can be

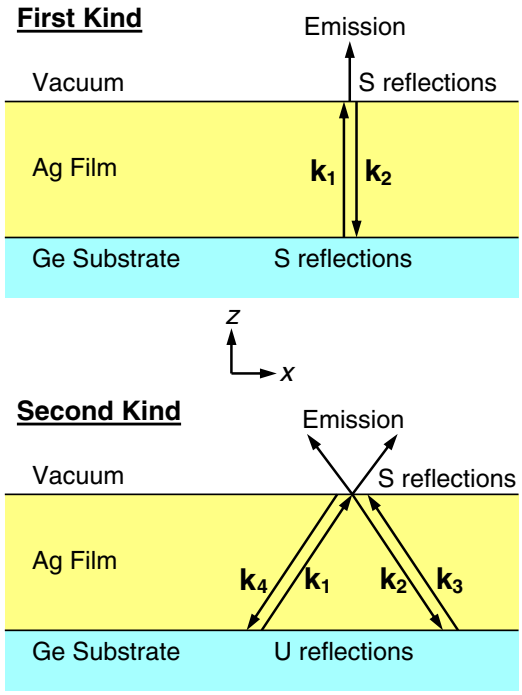

FIG. 1 (color online). Schematic ray diagrams for the interference paths corresponding to quantum well states of the first kind (top panel) and the second kind (bottom panel). The first kind involves two *S* reflections, one each at the surface and the interface, while the second kind involves two *S* reflections at the surface and a pair of conjugate *U* reflections at the interface.

diffracted into nonspecular directions via umklapp processes. As shown in the diagram, two conjugate umklapp retroreflections (U reflections) at the interface interlaced by two S reflections at the film surface can restore the phase of the electron wave. The resulting standing wave or quantum well state can be observed near a specific direction corresponding to the periodicity of the Ge(111) substrate surface. Both kinds of quantum well states can coexist in a film, as is the case for the system under study.

Angle-resolved photoemission is the best method for mapping the electronic structure of a film and is employed in the present study. The experiment was performed at the Synchrotron Radiation Center, University of Wisconsin-Madison, using 50 eV photons. Dispersion relations were measured along the $\bar{\Gamma}\bar{M}$ direction of the Ag(111) films, which is equivalent to the $[11\bar{2}]$ direction in bulk Ag. Photoelectron spectra were recorded as two-dimensional images with the energy and the polar emission angle θ as two independent variables. Each image spanned a range of $\Delta\theta$ of about 10°. The sample was rotated relative to the analyzer in steps of 5° to create a set of overlapping images, which were combined to create a wider angular span. A clean Ge(111)-$c(2 \times 8)$ surface was prepared by sputtering at a substrate temperature of 500 °C followed by annealing at 600 °C. Ag was evaporated onto the Ge substrate maintained at 50 K. Subsequently, the sample was annealed at 300 K and cooled back to 50 K for the photoemission measurement. The resulting Ag films, with bulk-like lattice constants, were oriented along (111) with the $\bar{\Gamma}\bar{M}$ direction parallel to the same in the substrate [17]. Atomically uniform films were prepared by carefully controlling the amount of deposition; the absolute film thicknesses were determined by atomic layer counting [1,18].

Results taken from a film with a uniform thickness of $N = 13$ monolayers (ML) are shown in Fig. 2 as a gray scale map. The vertical axis is the energy, and the horizontal axis is the in-plane momentum of the photoelectron, $k_{\|}$, calculated from the polar emission angle. The bottom panel of Fig. 2 reproduces the photoemission data presented in the top panel, overlaid with labels and results from model calculations. Near normal emission, or $k_{\|} = 0$, one observes a surface state band (SS) near the Fermi level ($E = 0$) and several approximately parabolic bands, labeled $Q1$, $Q2$, and $Q3$, which correspond to quantum well states of the usual kind [18]. Additional states of the series are also present in the data, but are much weaker. The dispersion of each state shows a break at the Ge valence band edge. This edge is indicated by the dotted curve derived from a band structure calculation [19]. The break is caused by a hybridization interaction of the quantum well state with the Ge substrate states [18,20,21]. A vertical dashed line at $k_{\|} = 0.907$ Å^{-1} indicates the location of the $\bar{M}$ point of the Ge surface Brillouin zone, where quantum well states of the second kind are expected. Indeed, the data show a series of approximately parabolic bands centered about this point. The curves shown in the lower panel are results from a model calculation. The observed states are located above the Ge valence band edge except the lowest one or two. The ones below the band edge are not fully confined by the substrate, and are expected to get broader and weaker at lower energies.

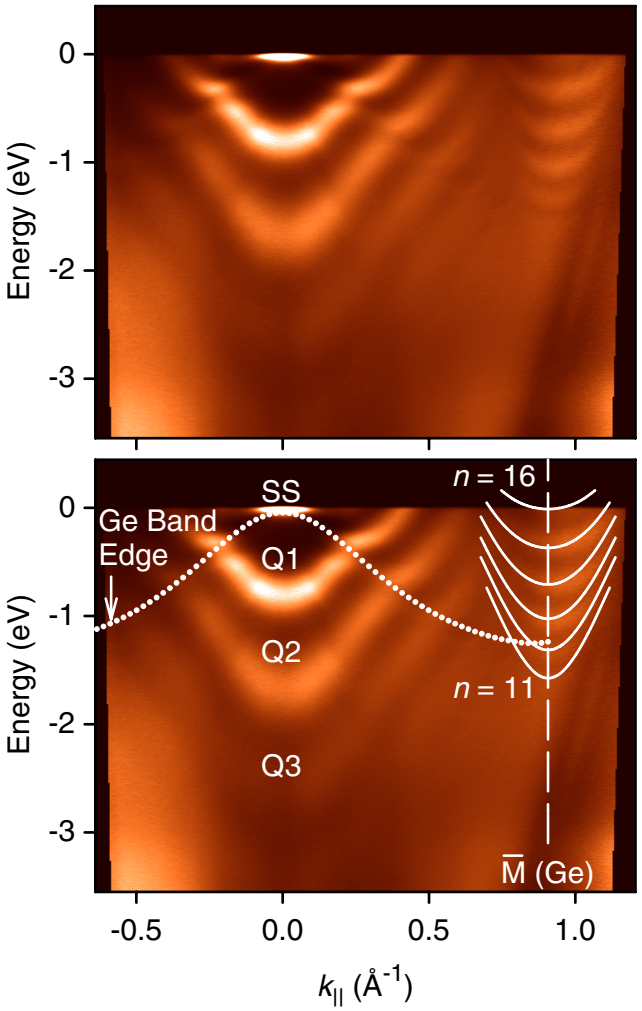

FIG. 2 (color online). Angle-resolved photoemission data taken from a 13 ML Ag film on Ge(111) (top panel) and the same overlaid with labels and results from a model calculation (bottom panel). The set of approximately parabolic bands centered about the $\bar{M}$ point of Ge are quantum well states of the second kind. The quantum numbers n are indicated. $Q1$, $Q2$, and $Q3$ are quantum well states of the first kind. SS is a Shockley surface state.

Quantum well states of the first kind can, in some cases, develop unusual dispersions due to band structure effects [22]. To verify that this is not the cause for the observed bands, we present in Fig. 3 a calculated projected bulk band structure along the direction of interest for a Ag(111) slab of a thickness of 13 ML [23,24]. Note the large difference between the $\bar{M}$ points of Ag and Ge. The dense set of states at energies -4 to -7 eV is derived from the Ag d states. Near the zone center at $\bar{\Gamma}$ and above the d states, there are several approximately parabolic bands which correspond to quantum well states of the first kind.

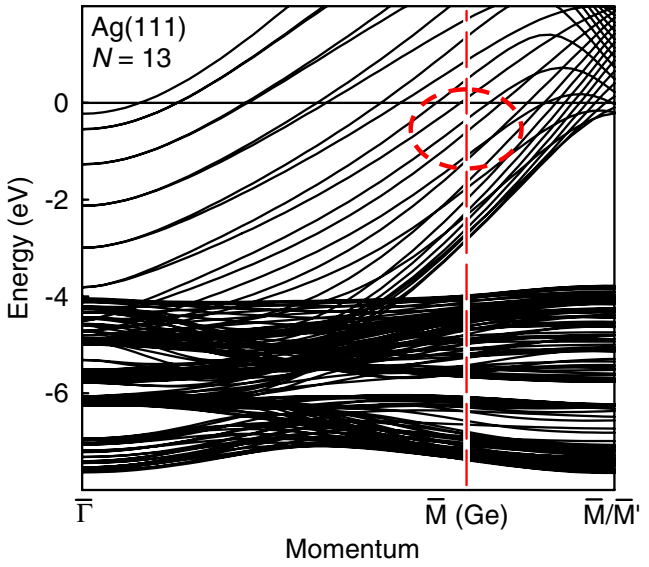

FIG. 3 (color online). Projected bulk band structure of a 13 ML Ag(111) slab. The region of interest where quantum well states of the second kind are expected is indicated by a dashed circle. The dispersion curves do not resemble the observed ones.

The energy positions and the band shapes resemble the experimental data; the differences can be attributed to boundary effects for the supported film. These bands extend into the region of interest indicated by the dashed circle, and their dispersions do not resemble the experimental results. Evidently, the observed quantum well states near $\bar{M}$ of Ge cannot be explained within the standard picture.

Referring to Fig. 1 for the second kind, two U reflections and two S reflections are required to complete the interference path. Four wave functions with distinct wave vectors are involved in the process. Define the coordinate system with the x axis along the in-plane direction of interest and the z axis along the surface normal. The four wave vectors are given by $\mathbf{k}_1 = (k_x, k_{1z})$, $\mathbf{k}_2 = (k_x, k_{2z})$, $\mathbf{k}_3 = (k_x - g, k_{3z})$, and $\mathbf{k}_4 = (k_x - g, k_{4z})$, where g is the magnitude of the relevant surface reciprocal lattice vector of Ge; $g/2$ is the distance between $\bar{\Gamma}$ and $\bar{M}$ of Ge. While a S reflection preserves k_x, a U reflection changes k_x to $k_x - g$, and a conjugate U reflection restores it back to k_x. The energies of the four wave functions must equal:

$$E(k_x, k_{1z}) = E(k_x, k_{2z}) = E(k_x - g, k_{3z}) = E(k_x - g, k_{4z}). \quad (1)$$

At each k_x and E selected by the photoelectron detector, the z components of the four wave vectors, k_{1z} through k_{4z}, can be determined from the bulk band structure $E(\mathbf{k})$ of Ag.

Referring to Fig. 1, $k_{1z} > 0$, $k_{2z} < 0$, $k_{3z} > 0$, and $k_{4z} < 0$ generally, but not always. The direction of interest $\bar{\Gamma}\,\bar{M}$ has a relatively low symmetry such that, in general, $E(k_x, k_z) \neq E(k_x, -k_z)$ and $E(k_x, k_z) \neq E(-k_x, k_z)$. Consequently, $k_{2z} \neq -k_{1z}$ and $k_{4z} \neq -k_{3z}$ in Fig. 1, despite that a S reflection is involved in each case. Rigorously speaking, S reflections in this system are not specular in that the incident and reflected wave vectors can make different angles relative to the surface normal due to the low symmetry. Likewise, the U reflections are not exactly retroreflections at $\bar{M}$ of Ge. The deviations are generally small but not necessarily negligible. These details are ignored in Fig. 1 for simplicity. For completeness of the discussion, we add that the band structure of Ag possesses inversion symmetry, $E(k_x, k_z) = E(-k_x, -k_z)$, because of time reversal symmetry and lattice inversion symmetry.

Coherent addition of wave amplitudes after four reflections as indicated in Fig. 1 leads to a stationary state, or a quantum well state. The phase of the wave function accumulates according to Bloch's theorem. The result is the following generalized Bohr-Sommerfeld quantization condition:

$$(k_{1z} - k_{2z} + k_{3z} - k_{4z})D + \Phi = 2n\pi, \quad (2)$$

where D is the thickness of the film, Φ is the sum of boundary phase shifts associated with the four reflections, and n is a quantum number.

The boundary phase shift Φ is unknown and can depend on k_x and E. To simplify the analysis, we introduce a charge spillage parameter Δ [25]. The idea is that the film is like a quantum box. The potential barrier is, however, not infinite, and the electron wave function can extend outward slightly beyond the box boundary, giving rise to a phase shift. Equation (2), within this approximation, becomes

$$(k_{1z} - k_{2z} + k_{3z} - k_{4z})(D + 2\Delta) = 2n\pi, \quad (3)$$

where Δ is the average charge spillage parameter per boundary (surface or interface), and is expected to be of the order of a fraction of a monolayer thickness. With this transformation, the boundary phase shift Φ in Eq. (2) is replaced by a geometrical phase shift $(k_{1z} - k_{2z} + k_{3z} - k_{4z})2\Delta$ in Eq. (3); this effectively changes the width of the quantum well from D to $D + 2\Delta$.

Solving Eqs. (1) and (3) numerically using an empirical band structure of Ag [23,24] yields the quantum well state dispersions shown in the lower panel of Fig. 2. The quantum number n for each observed band is indicated in the figure. The quantity Δ is treated as a fitting parameter. It is 0.31 in terms of the Ag monolayer thickness, a very reasonable value. The main effect of varying Δ is to move the bands vertically. The band spacings and the band curvatures from the calculation are in excellent agreement with the experiment. The band spacings are roughly one half of those for the quantum well states of the first kind because the interference path is roughly twice as long.

The observed band dispersions are symmetric about $\bar{M}$ of the Ge substrate, which is a telltale sign for the second kind nature of these quantum well states. This follows from

the fact that U reflections couple the states at k_x and $k_x - g$, and they must have the same energy. The state at $k_x - g$ must have the same energy as the state at $g - k_x$ by inversion symmetry of the band structure. Since the two momenta k_x and $g - k_x$ are symmetrically located about $k_x = g/2$, or $\bar{M}$ of Ge, the band dispersion must be symmetric with either a maximum or minimum located at $\bar{M}$. A related argument shows that quantum well states with the same dispersions must also be present on the left side of Fig. 2. This is indeed the case as verified by experiment (data not shown). By extension, quantum well states of the second kind should be present at locations associated with other Ge surface reciprocal lattice vectors. Access to these points, however, requires a substantially larger emission angle or a much higher photon energy. Our search for such emission features elsewhere has been hampered by the physical limitations of our setup and the diminishing photoemission intensity. No evidence has been found for any features that might be associated with the $c(2 \times 8)$ reconstruction of the clean Ge(111) surface [26].

In conclusion, we report on the observation of a new kind of quantum well state in an incommensurate thin film system. Ultrathin films will likely play an important role in future device designs. At the nanoscale, the coherence length of the valence electrons in metals can far exceed the dimensions of the system, giving rise to quantum coherence and interference effects. Diffractive effects, or U reflections, at an incommensurate interface can be important, as demonstrated in this work. Quantum well states of the second kind can give rise to important contributions to the system free energy and the overall electronic structure. Their possible impact on thin film science and technology is yet to be explored.

This work is supported by the U.S. Department of Energy, Division of Materials Sciences (Grant No. DEFG02-91ER45439). We acknowledge the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. National Science Foundation (Grant No. DMR-05-03323), for partial support of the synchrotron beam line operations. The Synchrotron Radiation Center of the University of Wisconsin–Madison, where this work was carried out, is supported by the U.S. National Science Foundation (Grant No. DMR-00-84402).

[1] T.-C. Chiang, Surf. Sci. Rep. **39**, 181 (2000).
[2] S.-Å. Lindgren and L. Walldén, *Handbook of Surface Science*, Electronic Structure Vol. 2, edited by S. Holloway, N. V. Richardson, K. Horn, and M. Scheffler (Elsevier, Amsterdam, 2000).
[3] M. Milun, P. Pervan, and D. P. Woodruff, Rep. Prog. Phys. **65**, 99 (2002).
[4] L. Aballe, C. Rogero, and K. Horn, Phys. Rev. B **65**, 125319 (2002).
[5] R. K. Kawakami, E. Rotenberg, H. J. Choi, E. J. Escorcia-Aparicio, M. O. Bowen, J. H. Wolfe, E. Arenholz, Z. D. Zhang, N. V. Smith, and Z. Q. Qiu, Nature (London) **398**, 132 (1999).
[6] F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis, Adv. Phys. **47**, 511 (1998).
[7] J. J. Paggel, T. Miller, and T.-C. Chiang, Science **283**, 1709 (1999).
[8] Umklapp reflections at a surface or interface involve a nonzero in-plane reciprocal lattice vector, and the geometry is generally not specular. Retroreflections refer to cases where the direction of the reflected wave is antiparallel to the direction of the incident wave. Umklapp reflections are well-known in low energy electron diffraction. Other examples of surface and bulk umklapp effects include the electronic structure of a modulated surface as reported by J. Lobo, E. G. Michel, A. R. Bachmann, S. Speller, J. Kuntze, and J. E. Ortega, Phys. Rev. Lett. **93**, 137602 (2004), and the electronic structure of a superlattice as reported by T. Miller and T.-C. Chiang, Phys. Rev. Lett. **68**, 3339 (1992).
[9] D.-A. Luh, T. Miller, J. J. Paggel, M. Y. Chou, and T.-C. Chiang, Science **292**, 1131 (2001).
[10] J. J. Paggel, C. M. Wei, M. Y. Chou, D.-A. Luh, T. Miller, and T.-C. Chiang, Phys. Rev. B **66**, 233403 (2002).
[11] T. Valla, M. Kralj, A. Siber, M. Milun, P. Pervant, P. D. Johnson, and D. P. Woodruff, J. Phys. Condens. Matter **12**, L477 (2000).
[12] D.-A. Luh, T. Miller, J. J. Paggel, and T.-C. Chiang, Phys. Rev. Lett. **88**, 256802 (2002).
[13] Y. Guo, Y.-F. Zhang, X.-Y. Bao, T.-Z. Han, Z. Tang, L.-X. Zhang, W.-G. Zhu, E. G. Wang, Q. Niu, Z. Q. Qiu, J.-F. Jia, Z.-X. Zhao, and Q.-K. Xue, Science **306**, 1915 (2004).
[14] T.-C. Chiang, Science **306**, 1900 (2004).
[15] M. M. Özer, J. R. Thompson, and H. H. Weitering, Nature Phys. **1**, 117 (2005).
[16] D. Eom, S. Qin, M.-Y. Chou, and C. K. Shih, Phys. Rev. Lett. **96**, 027005 (2006).
[17] L. Basile, H. Hong, P. Czoschke, and T.-C. Chiang, Appl. Phys. Lett. **84**, 4995 (2004).
[18] S.-J. Tang, L. Basile, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **93**, 216804 (2004).
[19] D. A. Papaconstantopolous, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).
[20] I. Matsuda, T. Ohta, and H. W. Yeom, Phys. Rev. B **65**, 085327 (2002).
[21] L. Aballe, C. Rogero, P. Kratzer, S. Gokhale, and K. Horn, Phys. Rev. Lett. **87**, 156801 (2001).
[22] M. H. Upton, T. Miller, and T.-C. Chiang, Phys. Rev. B **71**, 033403 (2005).
[23] N. V. Smith and L. F. Matheiss, Phys. Rev. B **9**, 1341 (1974).
[24] N. V. Smith, Phys. Rev. B **9**, 1365 (1974).
[25] P. Czoschke, H. Hong, L. Basile, and T.-C. Chiang, Phys. Rev. B **72**, 035305 (2005).
[26] Based on work on similar systems, the $c(2 \times 8)$ reconstruction, being an adatom-decorated structure, is unlikely to survive the deposition of Ag. See R. D. Aburano, H. Hong, J. M. Roesler, K. Chung, D.-S. Lin, P. Zschack, H. Chen, and T.-C. Chiang, Phys. Rev. B **52**, 1839 (1995).